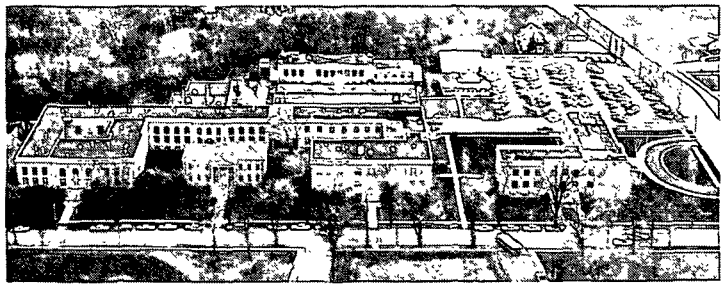

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CORROSION IN THE PULP AND PAPER INDUSTRY

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ABSTRACT

Equipment used in the production of pulp and paper products is affected by a variety of corrosion-related problems. Included among these problems are corrosion of recausticizing equipment, stress corrosion cracking of continuous digesters, bleach plant washer corrosion, suction roll cracking, feedwater deaerator storage tank cracking, recovery boiler tube corrosion, electrostatic precipitator corrosion, and corrosion of electronic equipment. Many of the corrosion problems affecting this industry have been resolved, in some cases by application of some of the most sophisticated control methods available to the corrosion engineer. These include anodic protection, weld overlays, thermal spray coatings, and the selective use of exotic alloys and fiber-reinforced polymeric materials.

INTRODUCTION

Few industrial plants can match the diversity of severely corrosive environments found in the typical pulp and paper mill. Pulp and paper mills routinely face corrosive environments ranging from hot alkaline sulfide cooking liquors to acidic, highly oxidizing bleaching solutions. Molten salts attack waterwall tubes in chemical recovery boilers, and condensates from flue gases attack electrostatic precipitator internals. Paper machine components are affected by localized corrosion, fatigue and corrosion under biological deposits. Erosion-corrosion affects the lifetime of woodyard equipment, refiner plates, and equipment for handling abrasive lime mud slurries. Indeed, pulp and paper mills are routinely challenged by virtually every known type of corrosion-related damage.

The annual cost of corrosion in the pulp and paper industry has been estimated at several hundred million dollars, not including the high cost of lost production due to corrosion-related downtime. In 1974, Davy and Mueller[1] estimated that each ton of bleach kraft paper product produced in North America incurred a five dollar cost attributed to corrosion control expenditures. A large mill producing 1000 tons per day would spend $5000 per day to accommodate corrosion-related damage, corresponding to more than $1.5 million per year. In 1984, more than 75 million tons of pulp-related products were produced[2], and, at $5/ton, it is clear that the industry faces a staggering cost burden approaching a half billion dollars. Moreover, lost production caused by corrosion-related downtime on critical equipment can easily amount to $500,000 per day. Finally, the human costs associated with catastrophic failure of corrosion-damaged equipment are beyond measure.

In view of the costs associated with corrosion, it is not surprising that the pulp and paper industry has often been at the forefront of corrosion control technology. This industry was one of the first to utilize molybdenum-bearing stainless steels more than 60 years ago, and the enthusiastic acceptance of FRP construction in the pulp and paper industry is well known. More recently, anodic and cathodic protection have been used to advantage in corrosion control in selected pulp and paper mill applications.

The objective of this article is to review corrosion-related problems in the pulp and paper industry. In recent years, a number of corrosion-related problems have emerged which impose heavy cost penalties on the industry. On the other

hand, new developments in corrosion control technology have eliminated several chronic, previously intractable corrosion problems. Obviously, a complete review of corrosion control in the pulp and paper industry is beyond the scope of this article, but there are a number of review articles which adequately address the topic[3-5].

CORROSION IN CHEMICAL PULPING EQUIPMENT

Pulping Processes

Although pulp is produced by many different processes, the most severe corrosion problems arise in chemical pulping where fibers are released from wood chips and other fibrous raw materials by chemical digestion at high temperatures and pressures. Two chemical pulping processes in widespread use today are the sulfite and kraft processes. In the sulfite process, digestion is accomplished in a neutral or acidified sulfite/bisulphite cooking liquor at elevated temperatures and pressure, whereas kraft pulping is accomplished with an alkaline sulfide cooking liquor. Kraft pulping has largely supplanted sulfite pulping in North America because the pulping chemicals can be easily and economically recovered in the kraft process.

Mechanical and chemimechanical pulping also account for a large (and increasing) share of pulp production in North America. Mechanical pulping involves separation of fibers by mechanical abrasion against a roughened wheel or a refiner plate, usually at slightly elevated temperatures. In chemimechanical pulping, the wood or other raw material is pretreated with chemicals prior to the abrasion process.

The kraft pulping and chemical recovery processes are shown schematically in Figure 1[6]. In the kraft process, the cooking liquor is known as white liquor — a solution containing sodium hydroxide and sodium sulfide as the active pulping constituents, and carbonate, sulfate, chlorides and other sulfoxy compounds as minor constituents. Typical composition ranges for white liquor are given in Table 1. Lignin is dissolved from wood chips exposed to white liquor at temperatures on the order of 350°F. This digestion may be accomplished as a continuous process or a repetitive batch process. After digestion, the pulp is washed and separated from the weak black liquor filtrate that contains the organic products dissolved from the wood.

Kraft pulping chemicals are reclaimed by concentrating the spent black liquor and burning the concentrated liquor in a chemical recovery boiler. The black liquor is concentrated (60-70% solids) in multiple-effect evaporators. Soap by-products called tall oil are generally decanted from the black liquor at intermediate stages in the evaporation process. Heavy black liquor fired directly into the boiler is dried, pyrolyzed, and burned to produce steam and electrical power. Organic constituents are converted into combustible gases and a carbon char that reduces sulfoxy compounds to sulfide. The inorganic smelt remaining after combustion and reduction is discharged as a molten mixture of sodium carbonate, sodium sulfide, and other minor constituents.

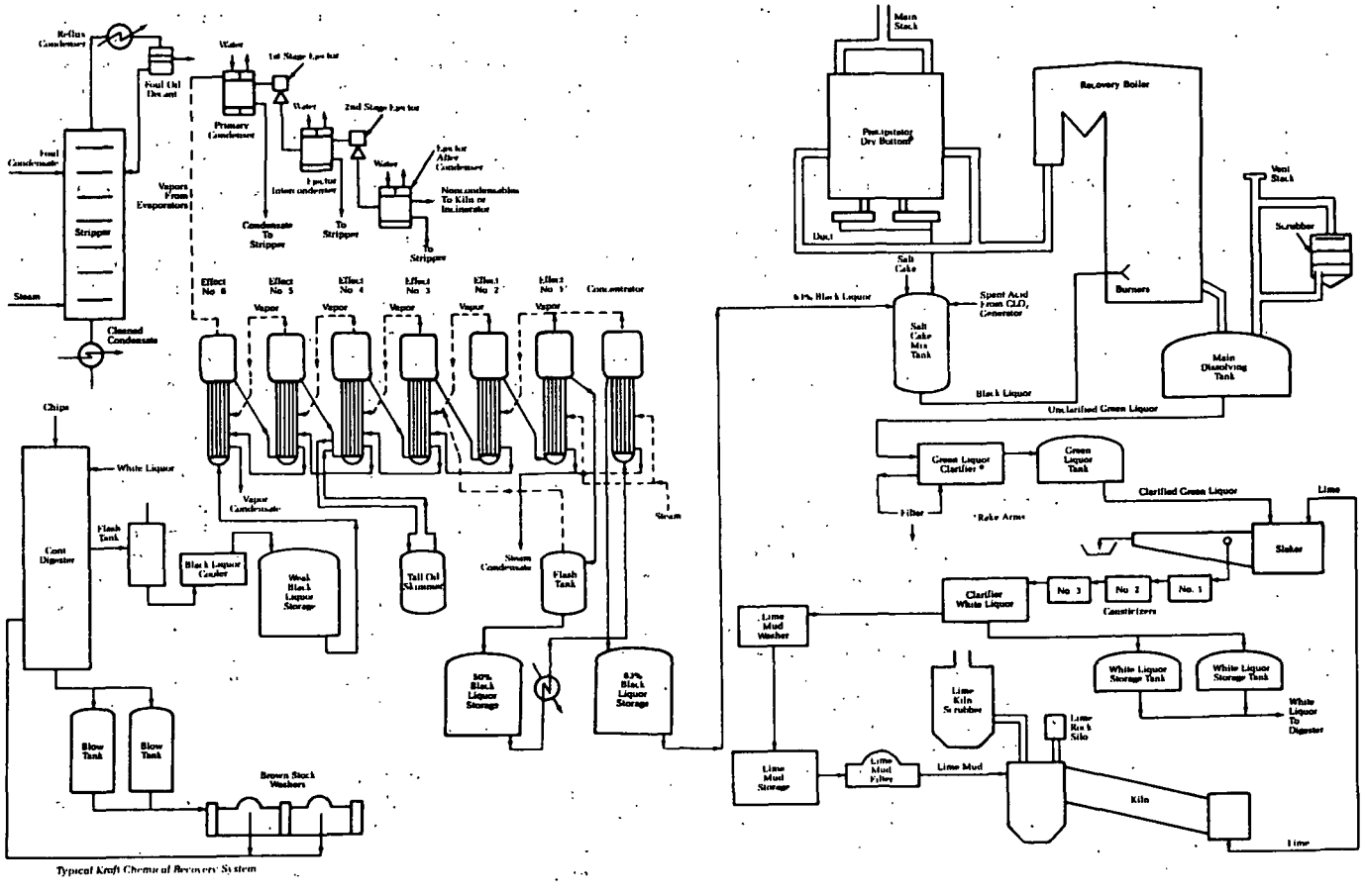


FIGURE 1—Kraft pulping and chemical recovery processes[6]

TABLE 1—Composition Ranges of Typical White and Green Liquors (g/L)

	NaOH	Na_2S	Na_2CO_3	Na_2SO_3	$Na_2S_2O_3$	Na_2SO_4	NaCl
White[1]	84-111	16-50	15-33	0.5-1.6	3.1-9.9	1.8-19.0	0.3-33.0
Green[2]	22-36	26-40	117-160	0.2-3.0	3.0-8.5	5.6-15.1	2.2-7.2

[1]Reference 7
[2]Reference 8

The molten smelt is dissolved and converted into white liquor by a process called recausticizing. Green liquor is formed when smelt is first dissolved in water (the green color comes from suspended ferrous corrosion products). The carbonates are converted to hydroxides by contact with slaked lime, according to the reaction

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow 2NaOH + Ca(CO_3)\downarrow$$

to form white liquor. The precipitated lime mud is reburned in a kiln to form lime for slaking.

Sulfite Pulping Processes

In sulfite pulping, elemental sulfur is burned to form sulfur dioxide which is converted to sodium, ammonium or magnesium sulfites and/or bisulfites, depending on the process used. Pulping is accomplished by digestion in the sulfite/bisulfite liquor at elevated temperatures, either as a batch or continuous process. The pulp is washed and separated from the spent sulfite liquor, (known as red liquor). Difficulties in reclaiming pulping chemicals from red liquor present economic and environmental obstacles to the use of the sulfite pulping process, although several sulfite mills remain in operation.

Corrosion Concerns in the Kraft Pulping Process

Each stage of the kraft process — pulping, recovery and recausticizing — is beset with severe corrosion concerns because of the aggressiveness of the white, green and black liquors toward plain carbon steel. Although 18Cr-8Ni stainless steels are usually fully resistant to corrosion by kraft liquors, most of the equipment in contact with kraft liquors is plain carbon steel for economic reasons. Corrosion and corrosion-assisted cracking of carbon steel equipment extract a heavy toll on kraft mill equipment. Some recent developments in corrosion control in kraft pulping operations are described below.

Stress Corrosion Cracking of Continuous Digesters. Stress corrosion cracking of continuous digester weldments became a serious problem in the 1980's, following catastrophic failure of a pressure vessel weakened by extensive stress corrosion cracking of girth welds.[9] An example of this type of weld cracking is shown in Figure 2. Examination of the ruptured vessel showed that the welds in the upper portion of the continuous digester vessel were damaged by extensive intergranular cracking. Careful inspection of welds in more than 100 vessels of similar design in operation in North America revealed that nearly half were severely cracked and required repairs[10]. About 20% of the digesters exhibited no cracking at all, in spite of similarity in design, fabrication and operation among cracked and uncracked digesters.

FIGURE 2—Stress corrosion cracking in the wall of a Kamyr continuous digester pressure vessel

A thorough investigation failed to uncover the reason for cracking susceptibility in some digesters and apparent immunity to cracking in others[10]. Complete stress relief prior to service minimized, but did not eliminate, susceptibility to cracking at the weldments. Vessels with higher rated capacities were somewhat more likely to experience cracking. Cracking susceptibility was unrelated to details of vessel fabrication, composition of liquors used in pulping, wood species pulped, age of the digester, acid cleaning practice, and other variables that might have affected cracking susceptibility. Chemical analyses of cooking liquors also failed to reveal differences linked to cracking susceptibility.

Laboratory and field studies indicated that the digester cracking phenomenon was a form of caustic cracking that occurred only in a very narrow potential range. Cracking similar to digester cracking was reproduced in the laboratory with slow strain rate tests conducted under controlled potential conditions in real and simulated cooking liquors[11-12]. Figure 3 shows branched intergranular cracking in a plain carbon steel SSRT specimen tested at a potential of -693 mVSHE in a liquor extracted from an operating continuous digester. The potential range for cracking of carbon steel in cooking liquors was only about 100 mV wide, ranging from -610 to -710 mVSHE. Cracking characteristics were largely unaffected by differences in cooking liquor composition and the composition or microstructure of the plain carbon steel.

The narrow potential range for cracking was consistent with predictions made by Parkins, Figure 4, who showed that the potential range for caustic cracking diminished drastically as the hydroxide concentration diminished toward 5%[13]. Although the caustic concentration in actual cooking liquors may fall below the 5% threshold for caustic cracking because of hydroxide reactions with wood, additional hydroxide is generated via hydrolysis of the sulfide

$$Na_2S + H_2O \longrightarrow NaOH + NaHS$$

It appears unlikely that the potentials of continuous digesters remain within the cracking range for prolonged periods. Tests conducted on an operating digester indicated that the digester potential during routine operating conditions was near, but not within, the potential range associated with cracking[12]. However, it was found that the digester potential did enter the cracking range and remained there for several days following a digester upset. Crack growth rate measurements in self-stressed specimens also support the contention that digester potentials generally remain outside the cracking range. The annual rate of crack growth in the controlled potential range is on the order of the typical digester wall thickness, whereas no growth rates that high have been inferred on operating digesters. If continuous digesters remained in the potential range for cracking, more rapid penetration of pressure vessel walls would be expected.

FIGURE 3—Branched intergranular cracking of a plain carbon steel specimen tested in a slow strain rate test

A number of remedial measures have been employed with varied success in eliminating continuous digester cracking[10]. In general, simple removal of cracks by grinding, or grinding followed by weld repair, has not reduced cracking susceptibility. In-situ stress relief has also failed to eliminate continued cracking. On the other hand, anodic protection and isolation of digester welds by weld overlays or sealed thermal spray coatings have generally been successful in suppressing further cracking. Cracking usually reappears when welds have been shot-peened for cracking control, but repetitive peening during successive semi-annual inspections has stopped cracking in some cases.

Barrier coatings consisting of high alloy weld overlays (placed in bands several inches wide over digester welds) are commonly used to protect carbon steel welds from cracking. Both high nickel alloys (e.g., Inconel 72) and stainless steels (e.g., 309, 310) have been used. The overlay alloys themselves are resistant to corrosion and cracking, but there have been reports of "ditching" due to galvanic attack of the carbon steel at the edge of the noble overlay coatings. There have also been reports of cracking of the carbon steel in the heat-affected zone at the edge of the overlay band[14], in some cases as deep as 3/8 inch. However, in most cases, high alloy overlay placed over digester welds has eliminated further cracking.

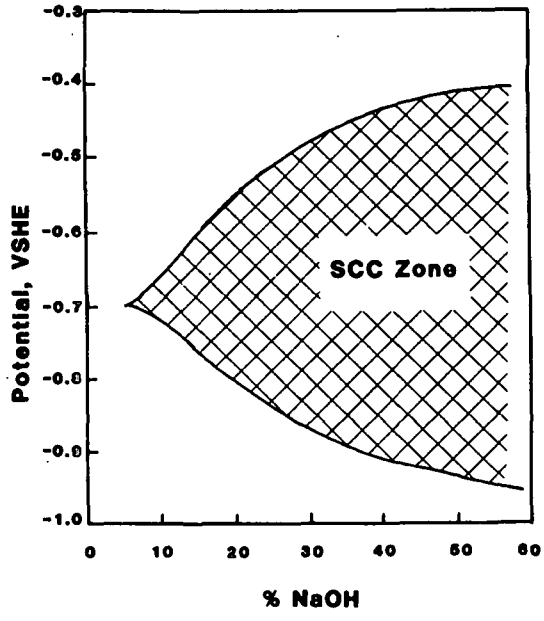


FIGURE 4—Potential dependence of caustic cracking of plain carbon steel (Ref. 13)

Sealed thermal-spray coatings have also been used successfully in protecting digester welds against caustic cracking in one digester[15]. After repair, high alloy coatings are applied over susceptible welds followed by application of a silicone-modified furan sealer. Unsealed plasma-sprayed coatings were unsuccessful when cooking liquor penetrated behind the coating and corrosion products delaminated the coating from the carbon steel substrate. The furan sealer prevents liquor penetration behind the thermal spray coating, while the porous coating anchors the furan sealer against the sloughing action of the chips in the digester. Sealed plasma-sprayed coatings have protected welds in one continuous digester for more than three years.

Anodic protection is currently being used in eight continuous digesters to prevent cracking and the localized corrosion that is occasionally found on digester walls[16]. A hollow cathode is installed concentric to the downcomer pipe in the impregnation zone of the digester, and a stainless steel pseudo-reference electrode is installed at a penetration through the digester wall. The digester is passivated by passing an initial current of approximately 1000A through the digester wall. The current required to maintain anodic protection is lower — on the order of a few hundred amperes. The digester is anodically polarized to the stainless steel potential — about 200 mV above the normal rest potential of the digester — which is well above the active/passive potential associated with cracking and pitting. In most installations, anodic protection was installed to eliminate localized corrosion on digesters without severe cracking and the approach has worked well. In the past two years, however, anodic protection has been used successfully to prevent further caustic cracking in two kraft digesters with severe, chronic cracking problems.

Thus, at least three alternative methods have been developed to prevent continued cracking of the continuous digesters used in kraft pulping. Each method has its advantages and disadvantages, and individual mills have adopted one or the other alternative based on mill priorities for cost, durability, and freedom from attention by mill personnel.

Anodic Protection of Recausticizing Equipment. General corrosion of steel equipment in the recausticizing plant is also a severe problem in many kraft mills. In most cases, clarifiers, storage tanks, piping, feedboxes and related equipment are fabricated from plain carbon steels such as AISI 1020 and A285-GrC. Stainless steel is used for some vulnerable equipment such as feedwells, clarifier rakes and rake arms and piping. Some mills have converted all recausticizing equipment to stainless steel to avoid corrosion problems in the recausticizing plant.

Corrosion rates as high as 20-30 mpy are experienced on the walls and trays of white liquor storage tanks and clarifiers where liquors are relatively stagnant. In piping and other locations where liquor velocity is considerably higher, corrosion rates as high as 200 mpy can be encountered. Corrosive attack is particularly severe on the walls of clarifiers and storage tanks where liquor levels fluctuate during routine operation. Similar rates of corrosion are encountered in green liquor process equipment.

The rate of corrosion of carbon steel exposed to white and green liquor is strongly affected by the composition of the liquor, particularly the thiosulfate and polysulfide concentration[17]. The rate of corrosion of plain carbon steel in binary hydroxide/sulfide liquor is relatively low over the range encountered in typical kraft white liquors — on the order of 5-10 mpy. However, thiosulfates present in white liquor raise the corrosion rate dramatically. As little as 10 g/L of $Na_2S_2O_3$ will double the corrosion rate, and 50 g/L of thiosulfate will raise the corrosion rate as high as 70 mpy. Polysulfides, Na_2S_x (x = 2 - 6), have a similar effect on corrosion rates when present in concentrations below 2.5 g/L, although higher corrosion rates appear to be transient. Since the polysulfides are strong oxidants, higher concentrations of polysulfide induce spontaneous passivation of carbon steel in white and green liquor. Other minor constituents of white liquor, such as carbonate, sulfite, sulfate and chloride, have negligible effects on corrosion rate of plain carbon steel in white and green liquor.

Although thiosulfates and polysulfides are known to accelerate corrosion of carbon steel recausticizing equipment, it is not a simple matter to reduce corrosion rates by excluding these species from the green and white liquors. Some sulfoxy compounds are present in the smelt as it leaves the recovery boiler. The weak wash liquor used to dissolve the smelt as it leaves the boiler may also contain some oxidized sulfur species. As a result, thiosulfate and polysulfide are usually present in recausticizing liquors from their inception. Moreover, the sulfides present in white and green liquor are readily oxidized when oxygen in the air contacts the liquor. Reducing corrosion rates by exclusion of oxidized sulfur compounds from white and green liquors is therefore not practical.

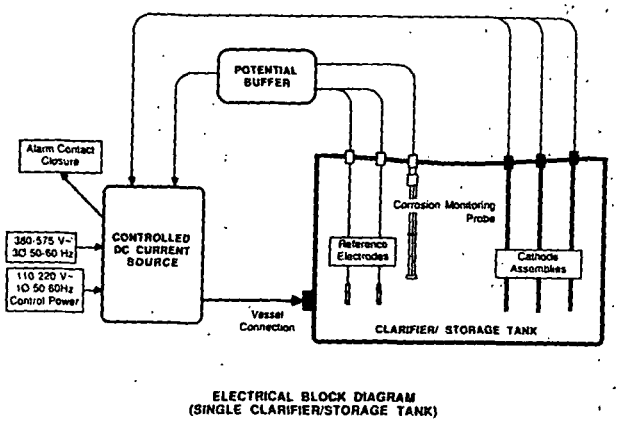
Several other alternatives have been used to limit corrosion of recausticizing equipment, with varying success. In some cases, clarifiers and storage tanks have been lined with epoxy or glass/epoxy composites. Although the epoxies have fair resistance to direct attack by white and green liquors, a more severe problem is penetration of liquor behind the epoxy. The corrosion products formed there tend to spall the liner from the wall within a few years of installation. A similar fate often befalls sprayed-on, alkaline-resistant concrete linings applied to the wetted surfaces of tanks and clarifiers. Although the concrete is resistant to direct attack by the liquor, penetration of liquor behind the lining often necessitates frequent maintenance. An enduring cure for severe corrosion at the liquid level line in tanks and clarifiers is the proper installation of a stainless or carbon steel "belly band" formed from plates welded to the inside of the vessel. Properly installed, each of a series of formed plates is seal-welded to the carbon steel vessel and then overlayed at the edges to form a continuous protective layer. A stainless layer offers an effective barrier to further corrosion. However, failure to seal weld each plate can lead to liquor penetration behind the stainless plates with rapid corrosion of the underlying carbon steel.

Within the past year, anodic protection has been developed as a corrosion control alternative for storage tanks and clarifiers in white and green liquor service[18]. Laboratory and field testing had shown that plain carbon steel in white and green liquor exhibits the active/passive transition required for anodic protection. An anodic shift in potential into the range, -510 to -585 mVSHE resulted in a tenfold reduction in the rate of corrosion. Potentials above -510 mVSHE could not be easily achieved because of the high current density associated with oxidation of a chemical species in the liquor. Presumably, sulfides are oxidized to polysulfide or thiosulfate. Peak passivation current densities were high compared to those encountered in continuous digesters, but the maintenance currents below -510 mVSHE were reasonably low.

In 1984 a prototype anodic protection system was installed to protect a large white liquor clarifier at the Weyerheauser mill in Springfield, Oregon (Fig. 5). This large single-tray clarifier had been experiencing severe corrosion at the liquid level, at rates averaging more than 25 mpy at the worst site. The clarifier had been scheduled for extensive repair or replacement. Instead, eight cathodes were suspended in the liquor from the roof, and a 1000A anodic protection system was installed to protect the vessel.

Startup of the anodic protection system occurred in December, 1984, with the use of four portable generators that provided a temporary boost in current to achieve initial passivation. Initially, 2000 amperes were applied to the vessel for 12 hours until a potential of -510 mVSHE was achieved. The estimated wetted surface area during initial passivation, including sidewalls, bottom tray and rake arms, was approximately 5×10^6 cm^2. Passivating current densities were therefore on the order of 0.4 mA/cm^2. This agreed well with the predicted critical current density found in stepwise polarization tests on carbon steel coupons previously aged in the white liquor at the

clarifier rest potential. Within days of passivation, the current drawn by the anodic protection system fell to a few hundred amperes at an applied voltage of one or two volts, for a total power consumption of a few hundred watts. This lower level of power consumption has remained more or less constant in the fourteen months since startup.



ELECTRICAL BLOCK DIAGRAM
(SINGLE CLARIFIER/STORAGE TANK)

FIGURE 5—Schematic diagram of the anodic protection system for a single tray clarifier

Tests have shown that anodic protection has suppressed corrosion on protected steel surfaces exposed in the clarifier. Corrosion coupons installed in the white liquor, with and without anodic protection at the clarifier potential, clearly showed a marked diminution of the rate of corrosion on protected coupons (Figure 6). The rate of corrosion on continuously immersed steel coupons was reduced by a factor of ten or more on protected coupons. At the wet/dry zone where liquor levels fluctuate, the level of protective was somewhat lower, but five-fold reductions in corrosion rates were evident. U-bend specimens suspended in the liquor, with and without protection at the clarifier potential, showed no evidence of stress corrosion cracking. Ultrasonic thickness measurements made on the clarifier wall before and after anodic protection also indicated that anodic protection of the wall was in effect, although the resolution of the ultrasonic measurements was limited.

Anodic protection extended to carbon steel surfaces below the lime mud sediment at the bottom of the clarifier, but did not extend along pipes into adjacent vessels. Clarifier potentials measured versus a reference electrode immersed in lime mud were virtually identical to those measured in the clarified liquor. Moreover, wall thickness measurements demonstrated that crevice corrosion did not occur in the extended crevice between the clarifier wall and the concrete/gravel pad supporting the bottom tray. There was no evidence of a shift in potentials of adjacent vessels when the anodic protection system was energized or switched off, indicating that the throw was limited by the 6-inch pipes entering the clarifier. Fortunately, the pipe runs where anodic protection ceased were made of stainless steel, which precluded accelerated corrosion where potentials fell below the critical potential.

Anodic protection proved to be an economical approach for corrosion control in recausticizing vessels such as storage tanks and clarifiers. The cost of anodic protection hardware is estimated at one-fourth of the cost of a replacement steel vessel, and one-eighth of the cost of a stainless steel vessel. More than five white and green liquor clarifiers are scheduled for anodic protection in 1986.

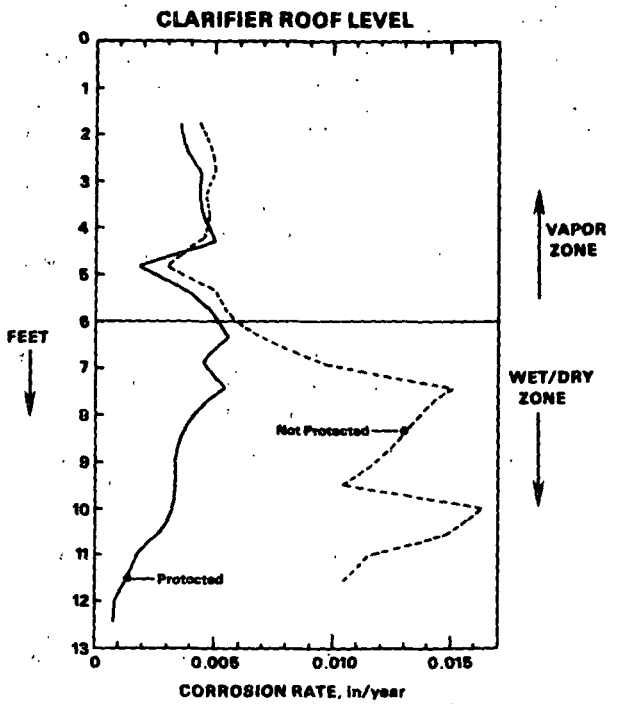


FIGURE 6—Anodic protection effectiveness on coupons installed in an anodically protected clarifier

Other Corrosion Concerns. Several other sites in the kraft pulp mill are afflicted by chronic corrosion problems, but most of these have been brought under control. Pitting and localized corrosion of batch digester walls is usually controlled by application of stainless weld overlays, although careful welding is required to maintain chromium levels sufficiently high to prevent cracking and/or pitting of the overlay itself. Duplex stainless steel tubes used in shell-and-tube liquor heaters have been effective in controlling corrosion and cracking often experienced by 18-8 stainless tubes. Duplex stainless steels (e.g., Ferralium 255) have also been effective in reducing errosion-corrosion caused by pulp impinging against target plates as batch digesters are blown free of pulp. Corrosion of fume hoods and ductwork on pulp washers, caused by volatile organic acids condensing on these surfaces, has been controlled by the use of FRP materials in these applications.

CORROSION CONCERNS IN KRAFT CHEMICAL RECOVERY

Black Liquor Processing

The process equipment used in recovery of pulping chemicals is affected by several chronic corrosion problems. Recovery equipment includes black liquor evaporators, storage tanks, black liquor oxidation apparatus, chemical recovery boilers, deaerators, and electrostatic precipitators.

Corrosion in multiple-effect evaporators is usually controlled by the use of stainless steels in critical, high temperature applications. The heat transfer surfaces are usually fabricated from 18-8 stainless steel in the highest temperature effects, with carbon steel finding application in lower temperature effects. Corrosion in evaporators usually occurs when hot black liquor inadvertently comes in contact with carbon steel surfaces because of foaming, excessive liquor throughput, and other operating misadventures. In most cases, the extent of corrosion is limited and can be controlled by application of stainless weld overlays or sealed thermal spray coatings.

Equipment in contact with black liquor at temperatures below 200°F can usually be constructed from plain carbon steel. Carbon steel storage tanks, piping, liquor oxidizers, etc., are generally resistant to corrosion by black liquors, except in those areas not washed by liquor, where volatile organic acids can condense. Roofs of carbon steel storage tanks are particularly susceptible to pitting by these condensed organic acids, but polymeric linings and FRP roofing are effective in controlling the problem.

Chemical Recovery Boilers

Chemical recovery boilers experience severe corrosion of carbon steel tubes in the waterwall above the char bed at the bottom of the furnace. Water-cooled smelt spouts used to discharge molten salts from the bottom of the boiler are also subject to severe corrosion and thermal fatigue failure. The mechanism of attack appears to be direct sulfidation of the steel by reduced sulfur species present in the lower zone of the furnace. Damage to waterwall tubes and smelt spouts is an abiding concern in the industry because of the potential for catastrophic steam explosions that can occur if these components leak and water contacts the molten salts in the smelt. The wastage of waterwall tubes is aggravated by higher tube wall temperature associated with the higher pressure boilers being installed in recent years.

Several different remedies have been used to control waterwall corrosion in recovery boilers, including the use of studded tubes, thermal sprayed coatings, and composite tubes. Boiler tubes are studded as shown in Fig. 7 to hold a layer of frozen smelt on the tube as an insulator against direct radiant heating from the char bed at the bottom of the furnace. The lower temperatures at the tube surface dramatically lower the rate of corrosion. Various thermal spray approaches have also been used to apply alloy coatings to the surfaces of boiler tubes, providing a barrier coating against sulfide attacks. Composite tubes of 304 L stainless steel coextruded over a carbon steel substrate also provide a barrier against direct sulfidation of the carbon steel tube. Although each of these remedies is widely used, the success of each approach has been limited by corrosion problems.

Composite tubes have the best history of resistance to fireside attack, particularly in Scandinavia where composite tubes have been used successfully for more than 15 years. Composite tubes are not without corrosion concerns, however. A particular concern has been burn-back of stainless steel at smelt spouts and air ports where poor heat transfer conditions raise the temperature of the stainless steel. Thermal fatigue has also been a serious problem in smelt spouts because of the fluctuating temperatures associated with erratic smelt discharge. Both of these problems — burn-back and thermal fatigue — have been addressed by design modifications. Within the last year, a third corrosion problem has surfaced in the form of wastage and cracking of stainless steel near air ports as shown in Figure 8. In spite of these problems and the considerable expense of composite tubes, they remain a popular corrosion control approach.

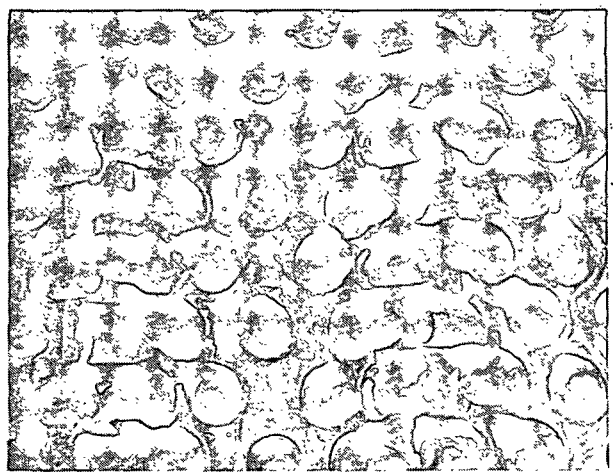


FIGURE 7—Recovery boiler tubes studded to retain a layer of frozen smelt against the tube, thereby insulating the tube and reducing corrosion

In past years, thermal spray coatings applied over waterwall tubes have not offered much protection against corrosion. The coating frequently spalled from the boiler tube surface soon after application, and little protection was provided. Sulfidation of nickel in the coatings was thought to be responsible for the poor durability. In recent years, plasma-sprayed Fe-Cr-Al alloys containing no nickel have been successful as barrier coatings in boilers where preceding generations of coatings had been largely unsuccessful[19].

There is, at present, no concensus regarding the optimum method for protection of waterwall tubes against fireside corrosion. Composite tubes offer a considerable improvement in resistance to fireside corrosion, but at considerable expense.

Few instances of superheater tube corrosion have been reported, which is not unexpected since chemical recovery boilers operate at lower pressures than utility boilers where such damage is prevalent. Superheater tube wastage in recovery boilers apparently occurs as a result of carryover of unburned black liquor droplets, and the

development of reducing conditions that destroy the magnetite film that normally protects the tubes.

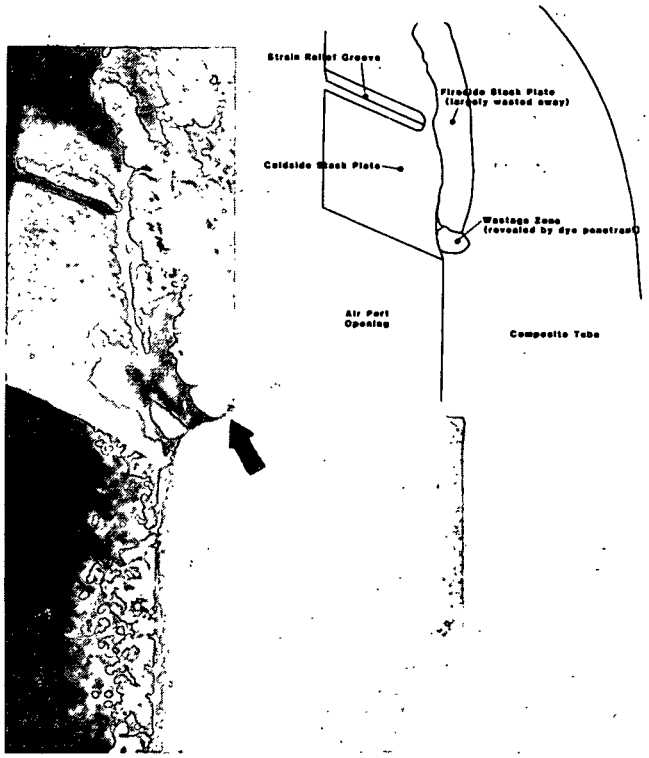


FIGURE 8—Recovery boiler tube wasteage in the stainless layer of composite tubes in the vicinity of a primary air port stack plate

Electrostatic Precipitators

Electrostatic precipitators are installed on chemical recovery boilers to recover saltcake particles entrained in the flue gas as it leaves the boiler. Failure to recover these particles would be a considerable economic burden in terms of lost chemicals, as well as an environmental concern.

Electrostatic precipitators that clean recovery boiler flue gases are susceptible to the same acid dewpoint corrosion that affects precipitators on power boilers[20]. Severe corrosion is found on sidewalls, collector plates, inlet and outlet baffles and ductwork, and other surfaces where flue gases stagnate, cool below the acid dewpoint, and precipitate corrosive acid films. Air in-leakage apparently compounds the corrosion problem. A recent TAPPI survey[20] found that as many as 70% of state-of-the-art precipitators experienced severe corrosion at some internal sites. Plain carbon steel and concrete, the most common materials of construction, are severely attacked by the sulfuric acid films that appear at lower temperatures.

The obvious remedy for flue gas corrosion is to maintain the flue gas temperature above the acid dewpoint, but this is difficult to achieve in practice since flue gas temperatures and dewpoint temperatures are not precisely known. Insulation of precipitator sidewalls and elimination of in-leakage of cool air appear to be beneficial. Heat-jacketing of precipitators is also effective to some extent, but the cost of heating is high. Few stainless alloys are resistant to the reducing mineral acids that precipitate in flue gas streams, but some polymeric coatings (furans and vinyl esters) have exhibited resistance to corrosion in this application. In spite of these control measures, precipitator corrosion continues to be a costly concern for the industry.

Deaerators

Recent discovery of widespread cracking in feedwater deaerators and deaerator storage tanks was precipitated by a catastrophic failure of a deaerator storage vessel in a U.S. linerboard mill[21]. Failure occurred when the head weld of a horizontal storage tank was compromised by subcritical crack growth. Inspection of the vessel following failure revealed extensive cracking at the welds in the storage tank and the deaerator itself. Cracks were straight, unbranched, and oxide-filled, and striations were found on the fracture surface indicating subcritical crack

Subsequent inspections revealed widespread cracking of a similar type in many other deaerators and deaerator storage tanks, not only in the paper industry, but also in several other industries, as well. A TAPPI survey indicated that 40% of carefully inspected deaerators had experienced the same type of cracking that had led to catastrophic failure[22]. Remedial measures have included vessel replacement, weld repair, shot peening, or stress relief.

CORROSION IN BLEACHING PROCESS EQUIPMENT

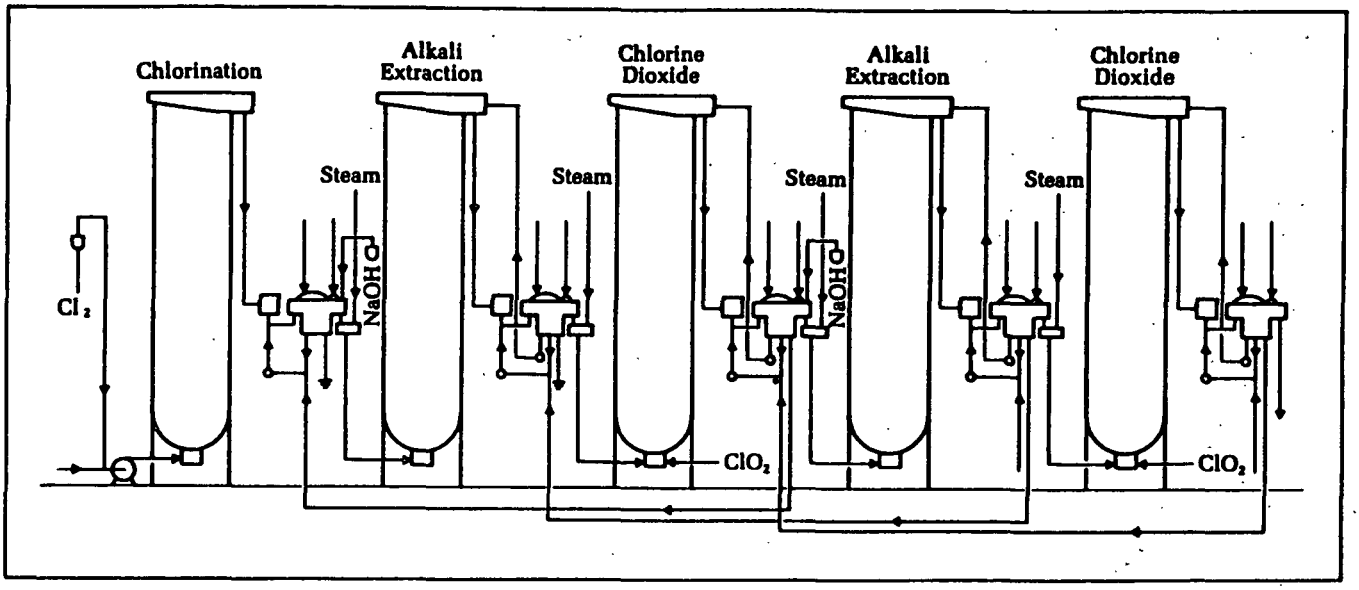
Bleaching Processes

Residual color in chemical pulp is usually removed by a multistep bleaching process shown schematically in Figure 9. The basic elements of the process are mixing, bleaching, washing, and caustic extraction (E) stages, arranged in one of a variety of sequences. The principal bleaching agents are chlorine (C), chlorine dioxide (D), and hypochlorite (H), although other chlorine-free bleaching agents such as oxygen (O) and peroxide (P) are gaining popularity. Usually, bleaching agents are mixed with the pulp before it enters bleaching retention towers. Bleached pulp leaving the tower is washed on a drum washer and then subjected to a caustic extraction (E) stage and a second washing stage. Several successive stages are usually involved in bleaching, designated as CEDEH or CEDED bleaching; the variety of bleaching sequences is endless.

Increasing closure of bleach plant operations has exacerbated corrosion damage in bleach plant equipment, particularly washer equipment. Closure is accomplished by increased water reuse and countercurrent washing, both of which increase dissolved and suspended solids and raise temperatures of washing stage filtrates.

Corrosion Concerns in Bleaching

Severe corrosion damage can occur in the bleach plants because of the strong oxidants used in the bleaching process. Care must be exercised in handling dry chlorine gas, and in generation of chlorine dioxide, to prevent catastrophic corrosion damage. In spite of the potential for severe



Flow Diagram of a Five-Stage Bleach Plant: CEDED

FIGURE 9—A typical multistage process for pulp bleaching[6]

corrosion, careful selection of corrosion resistant alloys and polymers has largely eliminated corrosion in the bleach preparation and handling stages.

Corrosion problems in bleaching towers have been overcome largely through the use of rubber, tile, or brickwork lining of mild steel vessels. Bleaching towers are usually fabricated from rubber-lined mild steel or acid-resistant brick/tile with polyester or silicate grouting. Extraction towers are usually lined with carbon or graphite brickwork and Portland cement or polyester mortars. Both types of tower perform well, although the maintenance costs associated with brickwork are often high.

Corrosion damage to bleaching stage washers, in the form of pitting, crevice corrosion and cracking, has proved to be more intractable. Filtrates from the C and D stages are very aggressive because of the low pH (less than 4 and often less than 2), high concentration of chlorine or chlorine dioxide carried over from the bleaching stage (< 2000 ppm), moderate chloride concentration (< 5000 ppm Cl^-) and moderate temperatures (50-70°C). Corrosion damage is less severe in the hypochlorite washers because the pH is higher. Corrosion concerns are so great in displacement bleaching equipment that complete titanium construction is required.

Increased bleach plant closure has led to degradation of molybdenum-bearing stainless steels, such as 316L and 317L, that had previously performed well in bleach plant washer applications. Several different approaches have been used in an attempt to reduce the rate of pitting and crevice corrosion in these washing stages. One approach has been the use of antichlor compounds that react with and remove residual chlorine from the pulp after bleaching but before washing stages. Other mills have employed more resistant materials, including proprietary stainless steels, titanium and FRP, or have turned to electrochemical protection. The optimum method of corrosion control is yet to emerge.

Bleach plant washer corrosion can be controlled through the use of exotic alloys, although the cost is relatively high[23]. A recent TAPPI survey[24] documented the corrosion resistance of exotic alloys. Titanium, for example, appears to be virtually immune to localized corrosion in bleach plant washers under routine conditions. Some of the high molybdenum alloys, such as Hastelloy® C276 and Inconel® 625 also provide good performance. The super-ferritic stainless steels, such as the 29-4 and 29-4-4 grades, are also resistant to localized corrosion but are limited in use by thin section sizes, high strength, and weldability concerns. Proprietary austenitic stainless steels containing 6% Mo, such as 254 SMO® and AL6XN, appear resistant to bleach plant corrosion while offering advantages in terms of cost, weldability and fabricability. In these applications, care must be taken to maintain high corrosion resistance of the base metal by using overmatching filler metals in welding.

Fiber reinforced polymerics also appear fully resistant to corrosion damage in bleach plant washers, and FRP coatings and linings have been widely used throughout the bleach plant for more than 40 years. Sharp and Nagaswami[25] have documented the extensive use of FRP coatings over stainless steel drums. Glass-reinforced vinyl esters and polyesters are used to encapsulate stainless drum washers. Lifetimes in excess of 20 years have been reported with FRP-lined washer drums in C and D stage service. In a few cases, monolithic FRP drums have been fabricated for use in washer stages and have performed well for nearly a decade.

An innovative, patented corrosion control approach involving limited cathodic protection has been used with success to protect stainless steel drums in bleach plant washer service[26]. Cathodic currents are impressed on the drum to lower the rest potential of the drum and increase the separation between the drum potential and its pitting potential in the washer filtrate, as

shown in Figure 10. A Pt-coated Nb anode is installed at the bottom of the vat. Cathodic protection instrumentation is used to depress the drum potential a few hundred millivolts. Significant reductions in metal loss have been reported with this protection scheme. However, occasional disruptions in protection have been experienced when platinum is lost from the anode. More than 70 bleach plant washers are currently protected by this form of electrochemical protection.

CORROSION DAMAGE IN PAPERMAKING EQUIPMENT

Papermaking Processes

Papermaking is a complex process involving many variations, but the underlying principle is simple — formation of a thin sheet of pulp slurry and extraction of the water. Most paper products are made on Fourdrinier machines, where pulp is discharged from a headbox onto an endless moving screen. Water is removed from the paper by gravity and vacuum until the consistency is high enough that the paper web will tolerate pressing and drying operations. In the press section, water is mechanically removed from the paper web as it passes through roll nips under high loads. Some of these press rolls — called suction press rolls — are perforated to apply a vacuum from an internal suction box to the paper web as it passes through the nip. Paper leaving the press section enters the dryer section, where the remaining moisture is removed as the paper passes over steam-heated dryer rolls.

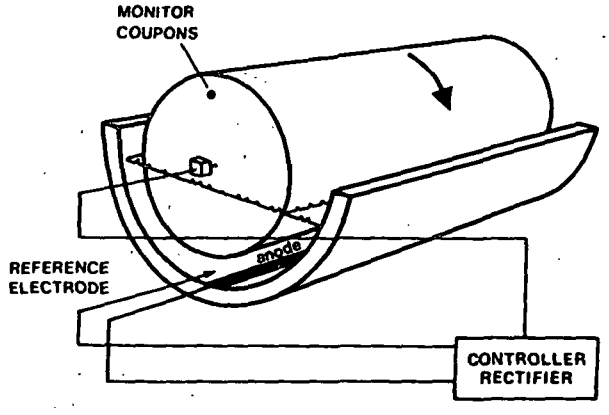


FIGURE 10—Electrochemical protection of a bleach plant washer drum

Papermaking involves extensive ancillary equipment for stock preparation and paper machine operation (Figure 11). Refiners are used to abrade fibers before papermaking so that they are softened and fibrillated to improve paper quality. Screens and centrifugal cleaners are used to remove undesirable particulates, while Deculators remove air from the stock before it enters the headbox. Fan pumps recirculate whitewaters needed for papermaking. Save-alls are filters used to retain fibers and other solids in the papermaking process. Liquid-ring vacuum pumps supply vacuum to various paper machine components. Nearly all of these components, as well as the paper machine components, are made from 18-8 stainless steel, although some bronze, cast iron, and FRP materials are found in contact with papermaking stock, as well.

Papermaking stock is treated with numerous additives to facilitate paper formation and reduce costs. Most paper is made using the alum-acid process, wherein alum is added to lower the pH of the stock and promote the precipitation of rosin sizing agents that control the wettability of the final paper product. Some paper is made by the alkaline process, wherein the stock is made slightly alkaline and synthetic sizing agents are used. Other additions may be made to control dewatering, retain brightness, improve wet strength, increase paper bulk, increase paper opacity, or control biological growths.

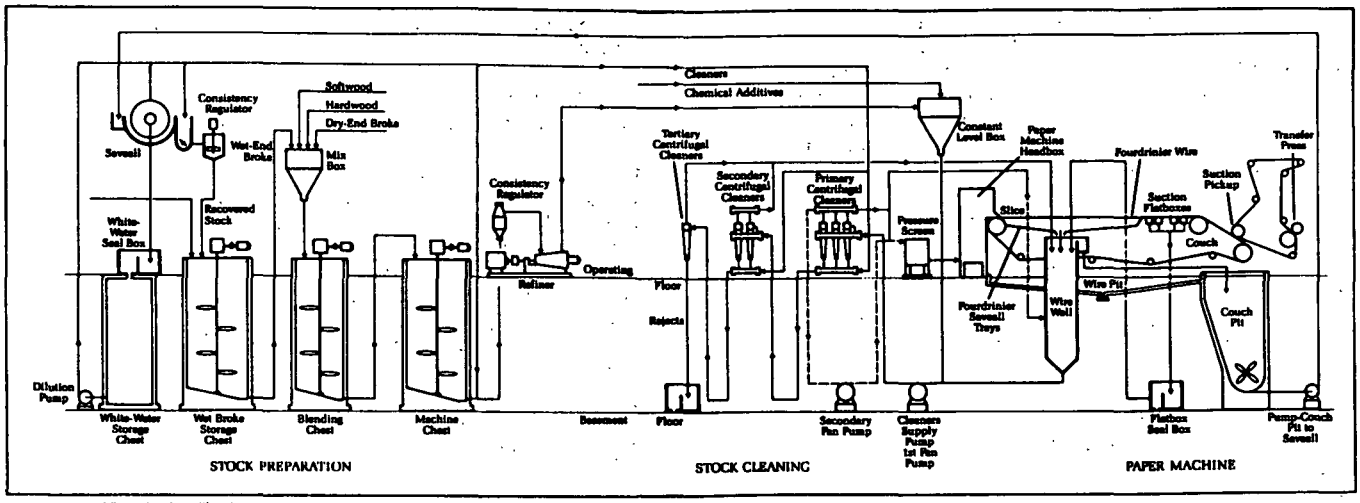
Paper machines have also been closed to a considerable extent during the past decade. Decreased freshwater usage and increased reuse of white water has raised temperatures, increased suspended and dissolved solids, and increased the propensity for biological growth. All of these factors have increased the corrosivity of paper machine white waters.

Corrosion Concerns in Papermaking Operations

Most of the equipment wetted by paper machine whitewaters is stainless steel (304L or 316L), FRP, tile and grout, or bronze, so general corrosion is usually not a concern. Equipment that is not wetted by whitewater directly, but may be affected by splashes or evaporation/condensation, is usually fabricated from materials with less corrosion resistance. Cast iron machine structures and carbon steel roof sections are particularly susceptible to corrosion in the vicinity of the paper machine.

Paper machine components are susceptible to crevice corrosion under deposits resulting from fiber poultices or biological growths, as shown in Figure 12. Critical equipment, such as headboxes and headbox internals, is often electropolished to minimize hang-up of fibers and adhesion of slime deposits. Careful biocidal treatment programs are necessary to prevent the growth of slimes and other biological deposits that can lead to crevice corrosion. FRP construction is effective in reducing crevice corrosion in piping and chests experiencing crevice corrosion.

In recent years, thiosulfate anions have been identified as a species promoting pitting and crevice corrosion of stainless steel equipment used in manufacture of certain grades of paper. Paper machines processing pulps produced by groundwood processes have been particularly susceptible, since the sodium hydrosulfite brighteners used on these pulps readily decompose into thiosulfate. Garner[27] has shown in laboratory tests that concentrations of thiosulfate as low as a few parts per million can induce pitting of type 304 and 304L stainless steels. Types 316 and 316L stainless steels are more resistant, but are not immune from such pitting. Pitting is more severe in whitewaters containing dilute concentrations of chloride in addition to thiosulfate. It is interesting to note that pitting does not occur when thiosulfates are present in larger amounts, apparently as a result of a disproportionation of thiosulfate that neutralizes acids in the pitting anolyte.



Typical Paper Machine Flow Diagram.

FIGURE 11—A typical paper machine flow diagram[6]

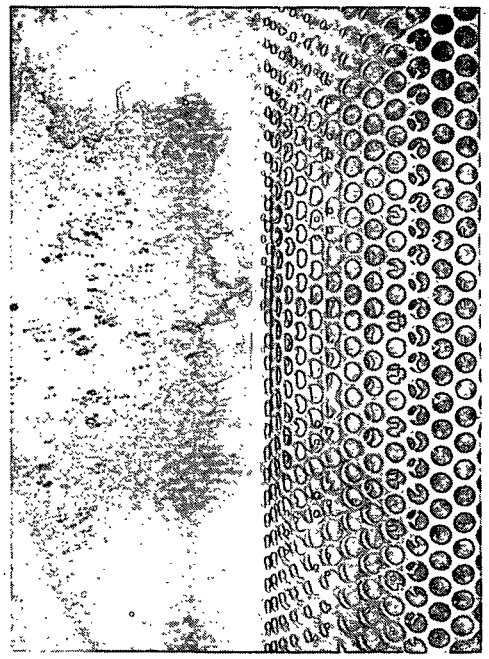


FIGURE 12—Pitting and crevice corrosion of a paper machine headbox

Thiosulfate-induced pitting can be controlled by removal of the aggressive anion or by use of more resistant type 316L stainless steel in white-water applications. Thiosulfate concentrations can be controlled by careful control of the pulp brightening process. Reducing hydrosulfite retention time, eliminating air contact, reducing hydrosulfite storage temperatures, and eliminating thiosulfate in hydrosulfite supplies can reduce thiosulfates to acceptable levels in whitewaters derived from groundwood pulps.

Suction roll cracking has continued as a serious problem in papermaking applications. Suction rolls are perforated rolls which impart a vacuum on the paper web from an internal suction box. Suction rolls are typically found on the last roll of a Fourdrinier paper machine (the couch roll) or in the press section. Cracking occurs by corrosion fatigue induced by the fluctuating stresses that are imposed during routine operation. Garner[28] reported more than 90 suction roll failures in Canadian mills over a ten year period. As shown in Figure 13, cracks typically begin on the inside surface of the roll at a drilled hole, and propagate from hole to hole to cause eventual failure of the roll. In many cases, multiple cracks have initiated and are propagating in a roll at any given time.

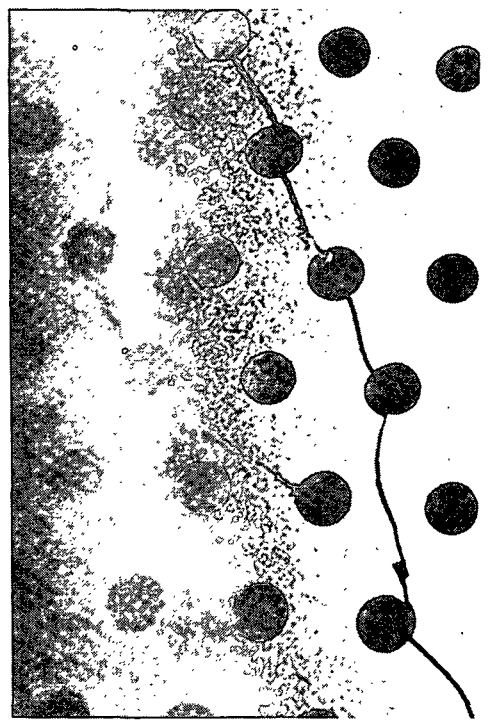


FIGURE 13—Cracking in a duplex stainless suction roll shell

Conditions have become more challenging for suction roll survival over the years. As paper machine widths increased, the distance between roll supports increased as well, leading to higher cyclic stresses. Bronze rolls used in narrow paper machines did not have the stiffness required for wider machines. Increased running speeds contributed to the demands on suction rolls as nip loads were raised to compensate for reduced nip residence times. Increased rotation speeds resulted in more stress cycles in a year of operation; suction rolls may experience 2×10^8 stress cycles in a year of operation. Increased whitewater corrosivity with increased closure also increased demands on suction roll alloys.

Suction roll metallurgy has developed rapidly in response to increased demands on suction rolls. A succession of stainless steel alloys have been used in suction roll applications. The first replacement for the bronze roll was the 13Cr stainless steel roll (CA 15), but this roll alloy experienced severe pitting and extensive cracking in service because of marginal corrosion resistance. Cast austenitic stainless steels were also used in suction roll applications, but sensitization associated with slow cooling often resulted in intergranular stress corrosion cracking[29].

Since the early 1960's, cast duplex stainless steel rolls have offered the greatest resistance to corrosion-assisted cracking, although immunity from cracking is still not available. The first commercially available suction roll alloys, such as Alloy 63 and KCR171, were solution treated and quenched during fabrication. The residual stresses accompanying this heat treatment have been implicated in the poor to fair corrosion fatigue resistance exhibited by these alloys. Current generations of cast duplex suction roll alloys have slow cooling heat treatments or aging heat treatments to minimize residual stress. These alloys, such as Alloy 75 and VKA 378, have much greater resistance to cracking than alloys used previously. However, these alloys have been used in suction roll applications for less than ten years, and it is premature to conclude that cracking has been eliminated.

Although most suction roll alloys are centrifugally cast, both forged and formed-and-welded rolls have been marketed in recent years. It is too early to determine whether the refinement in metallurgical structure of wrought alloys will result in improved resistance to corrosion-assisted cracking.

CORROSION OF ELECTRONIC EQUIPMENT

It is not surprising to learn that corrosion can degrade the performance of electrical and electronic equipment used in the pulp and paper industry. Low concentrations of aggressive gases are ubiquitous in the typical mill, including H_2S, SO_2, mercaptans and other reduced sulfur compounds from the pulping processes, and chlorine from bleach plant operations. These gases severely attack copper and silver conductors in electrical and electronic equipment. Digital equipment such as process control computers is particularly susceptible because of corrosion at edge connectors on circuit boards. Even though these connectors are typically electroplated with a thin layer of gold, sulfidation of the copper substrate occurs at pin-holes in the gold and the expansion of the CuS corrosion product forces electrical contacts apart.

Stringent limits on reduced sulfur concentrations in the atmosphere can eliminate service interruptions in electronic equipment, but careful precautions are required to achieve protection[30]. Target levels of H_2S for uninterrupted operation are as low as 3 parts per billion, compared to a few thousand ppb in the general pulp mill atmosphere. Such low levels can be achieved in control rooms and computer rooms by carefully sealing the room against invasion by corrosive gases, and installation of equipment to purify and dehumidify the air inside the room. The rate of growth of sulfide films falls dramatically in areas where these precautions are taken, and downtime of electronic equipment is reduced in proportion.

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